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(54) A fiber reinforced composite material.

(57) A fiber reinforced composite material is provided. This comprises:
(a) at least one composite material layer, which comprises reinforcing fibers impregnated in a constrained type vibrational damping resin material, and
(b) at least one composite material layer, which comprises reinforcing fibers impregnated in a resin material other than said constrained type vibrational damping resin material.

By introducing the layer (a), it becomes possible to absorb flexural vibration and obtain a large vibrational damping property independently of orientation angles of reinforcing fibers.

EP 0 439 197 A2

A FIBER REINFORCED COMPOSITE MATERIAL

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a fiber reinforced composite material which is effective to reduce vibration and noise when used for a construction body such as a space construction equipment, for example , an artificial satellite, an office automation machine and device, an automobile, a leisure article or the like.

Description of the prior art

Fiber reinforced composite materials are those comprising inorganic fibers such as carbon fibers or glass fibers or organic fibers such as aramid (= aromatic polyamide) fibers integrally combined with a matrix resin such as an epoxy resin, a polyimide resin or a polyether-ether keton resin.

Such fiber reinforced composite materials, when compared with conventional metal structural materials, have advantages of light weight and high strength and also an advantage that any desired mechanical properties can be obtained by appropriately controlling orientation angles of the fibers. Therefore, the fiber reinforced composite materials tend to be widely used for construction materials particularly for those requiring light weight, such as a space construction equipment, an aircraft, an automobile, a leisure article or the like.

As the use of such composite materials have been broadened, there occurs a problem of vibration.

Since the fiber reinforced composite materials are lightweight and have a small vibration damping property (of loss factor η = 0.001 - 0.01) to an extent similar to that of conventional metal construction materials, they are liable to vibrate. Further, they are often used for molding a construction body as a whole and so it is impossible to rely upon any vibration damping by friction at connecting portions (structural damping) differently from conventional metal structural materials. Therefore, in a space construction equipement such as an artificial satellite, problems of troubles of loaded apparatus and lowering of precision of antenna positions occur owing to the vibration of the construction body. It is thus very important to improve the vibration damping property of fiber reinforced composite materials.

As reported by K. Shimizu in "Composite Materials", K. Kawata & T. Akasaka, Ed., Proc. Japan - U.S. Conference, Tokyo, 1981, pages 111 - 118, it is possible to increase vibration damping of a composite material by incorporating a flexibility-attaching agent such as polyethylene glycol, polypropylene glycol or liquid rubber into a matrix resin of the composite material. The vibration damping property of the matrix resin itself can be much improved by such agent, but that of the composite material in its entirety can only slightly be improved by such agent. Further, the stiffness of the composite material is considerably decreased by such agent. The use of the flexibility-attaching agent therefore is not effective.

SUMMARY OF THE INVENTION

An object of the present invention is therefore to present a fiber reinforced composite material having a large vibration damping property.

The present invention thus provides a fiber reinforced composite material comprising:

(a) at least one composite material layer, which comprises reinforcing fibers impregnated in a constrained type vibrational damping resin material, and

(b) at least one composite material layer, which comprises reinforcing fibers impregnated in a resin material other than said constrained type vibrational damping resin material;

said composite material layers (a) and (b) being laminated and integrated.

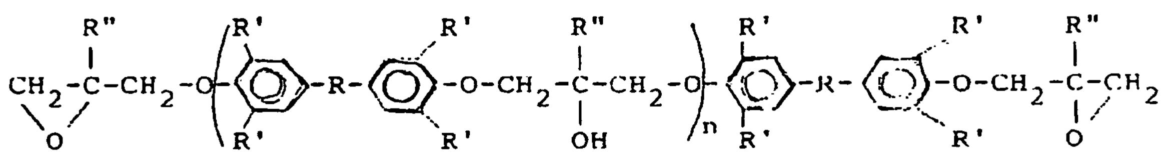
The constrained type vibrational damping resin material is one that is described in the present inventors' Japanese Patent Applications Nos. 18,912/87, 18,913/87, 92,688/87, 92,689/87, 59,866/87 and 31,415/88 and the corresponding European Patent Application No. 88 90 1307.4. Some of representative resin materials described therein are recited hereinafter.

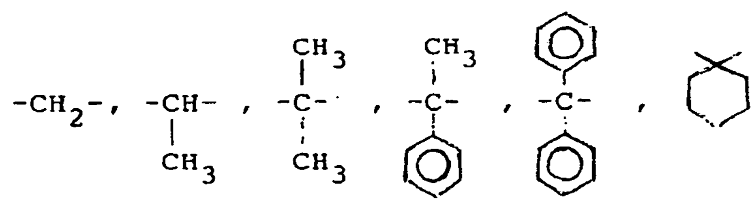
(1) A resin material containing (a-1) an epoxy resin, for example, glycidyl ether of bisphenol A, glycidyl ether of bisphenol F or glycidyl ether of bisphenol AD, (b) a curing agent, for example, amines, acid anhydrides, polyamides or dicyandiamido, and (c-1) a liquid polymer having in the molecule on the average more than 1.6 functional groups capable of reacting with the epoxy group of the epoxy type

resin, said functional group being at least one selected from the group consisting of carboxyl group, acid anhydride radical, acid amide radical, amino group and mercapto group, and a glass transition temperature of less than 0°C, for example, a butadiene/ acrylonitrile copolymer having carboxyl or amino terminals or a maleic anhydride-grafted ethylene/α -olefin copolymer.

(2) A resin material containing (a-2) an epoxy resin comprising glycidyl ether of polyol or its polymer, for example, ethylene glycol diglycidyl ether, diethylene glycol diglycidyl ether, dipropylene glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether or polytetramethylene glycol diglycidyl ether, (b) a curing agent and (c-2) a compound comprising a polymer consist essentially of aromatic hydrocarbons, phenols or at least one thereof and having a softening point of less than 25°C, for example, a condensate of xylene with formaldehyde, isopropenyltoluene polymer, phenol-modified aromatic polymerized oil, tricyclodedecene/toluene polymer or nonylphenol, the softening point of which is loss than 25°C.

(3) A resin material containing an epoxy resin (I) obtained by addition reaction of (a-3) a bisphenol type epoxy resin represented by the following general formula with (c-3) a cyclic ester at the (c-3)/(a-3) weight ratio of 20/80 to 98/2 and (b) a curing agent, the (b)/(I) equivalent weight ratio of said epoxy resin (I) to said curing agent (b) being in the range of from 0.6 to 1.4.





wherein R is
-O- or

$$-\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle O}{\|}}{S}}}-$$

, R' is hydrogen atom or halogen atom, R" is hydrogen atom or methyl and n is an integer of 1 or more provided that parts of whole of the benzene rings may be hydrogenated.

Examples of the bisphenol type resin (a-3) are glycidyl ether of bisphenol A, glycidyl ether of bisphenol F, glycidyl ether of 1,1-bis(4-hydroxyphenyl)ethane, glycidyl ether of 1,1-bis(4-hydroxyphenyl)cyclohexane, glycidyl ether of 1,1-bis(4-hydroxyphenyl)-1-phenylethane or glycidyl ether of (4-hydroxyphenyl)sulfone. Example of the cyclic ester (c-3) is β -propiolactone, δ -valerolactone or ϵ -caprolactone.

As for such constrained type vibrational damping resin material, it is preferable to use a material having an elastic modulus of not higher than 10 Kgf/mm^2 more preferably not higher 1 Kgf/mm^2 and a mechanical loss tan δ of not less than 0.1 more preferably not less than 0.5.

As for the resin material other than said constrained type vibrational damping resin material, it is possible to use a conventionial resin material used for a resin matrix of a fiber reinforced composite material, for example, a highly hard resin such as an epoxy resin (excepting the above mentioned constrained type vibrational damping epoxy resin), a polyimide resin or a polyether-ether keton resin.

As for the reinforcing fibers, any known reinforcing fibers, for example, inorganic reinforcing fibers such

as carbon fibers, alumina fibers, silicon carbide fibers or glass fibers and organic reinforcing fibers such as aramid fibers or TECHMYLON (trade name) can be used. These reinforcing fibers can be used in various forms, for example, unidirectionally aligned strands or rovings, a woven fabric of plain weave, twill weave, satin weave, etc., chopped short fibers, a non-woven mat-like fabric comprising intertwined fibers.

It is convenient and so is preferable to form the composite material layers (a) and (b) as prepreg sheets, respectively. Such prepreg sheets can be prepared by a method by itself known, that is, by impregnating reinforcing fibers in a matrix resin material and then semi-hardening the resin material.

The fiber reinforced composite material of the present invention can be produced by laminating at least one prepreg sheet for the layer (a) and at least one prepreg sheet for the layer (b) and integrating them by a moulding method by itself known, for example, an autoclave method or a hot-press method, but it is possible to form the layers (a) and (b) without using the prepreg sheets, that is, by applying the reinforcing fibers and the matrix resins to a mold in situ and integrating them as a laminated body.

In the fiber reinforced composite material of the present invention, the constrained type vibrational damping resin material in the layer (a) absorbs flexural vibration by its large shear deformation and enables to obtain a large vibrational damping property which is indepent of orientation angles of reinforcing fibers. Therefore, it becomes possible to elect numbers and positions of the layers (a) and (b), form and direction of the reinforcing fibers in the layers (a) and (b) and kind of matrix resins in the layers (a) and (b) so that the final product has desired properties of elastic modulus, tensile strength, etc., retaining its vibrational damping property at a constant high level.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a cross section of a prepreg sheet which is used to produce the layer (a) of a fiber reinforced composite material of the present invention.

Fig. 2 shows a cross section of a prepreg sheet which is used to produce the layer (b) of a fiber reinforced composite material of the present invention.

Fig. 3 shows a cross section of a first embodiment of a fiber reinforced composite material of the present invention produced by using the prepreg sheets shown in Fig. 1 and Fig. 2.

Fig. 4 shows a cross section of a second embodiment of a fiber reinforced composite material of the present invention.

Fig. 5 illustrates frequency characteristic curves of loss factors of the composite materials of the first and the second embodiments shown in Fig. 3 and Fig. 4 and a prior art composite material.

Fig. 6 shows a cross section of a third embodiment of the composite material of the present invention.

Fig. 7 illustrates frequency characteristic curves of loss factors of the composite material of the third embodiment shown in Fig. 6 and a prior art composite material.

Fig. 8 shows cross section of a fourth embodiment of the composite material of the present invention.

Fig. 9 illustrates frequency characteristic curves of loss factors of the composite material of the fourth embodiment shown in Fig. 8 and a prior art composite material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be explained below further in detail with respect to its some embodiments.

Referring to Fig. 1, by impregnating a carbon fiber plain weave fabric 2 with a constrained type vibrational damping epoxy resin 3 based upon a polyether type epoxy resin and semi-hardening the epoxy resin, a preprey sheet 1 is produced. This prepreg sheet 1 has a mechanical loss tan δ of 1.5 at a room temperature.

In the similar manner, a prepreg sheet 5 is produced from a carbon fiber plain weave fabric 2 and an ordinary epoxy resin 4, as shown in Fig. 2.

The prepreg sheets 1 and 5 are laminated and moulded into an integral body by an autoclave method. In a first embodiment shown in Fig. 3, two prepreg sheets 1 are sandwiched between upper three prepreg sheets 5 and lower three prepreg sheets 5 to form a composite material C1. In a second embodiment shown in Fig. 4, six prepreg sheets 5 are sandwiched between an upper single prepreg sheet 1 and a lower single prepreg sheet 1 to form a composite material C2. In both of the first and the second embodiments, all of the prepreg sheets 1 and 5 are laminated so that the carbon fiber fabrics may align in the same fiber directions.

Relation between loss factors and frequencies is determined by applying flexural vibration to test samples of the composite materials C1 and C2 produced as above and a test sample of a prior art composite material C3 produced in the similar manner but from only eight sheets of the prepreg sheet 5

shown in Fig. 2. The loss factors are obtained from free damping curves at characteristic frequencies of the composite materials. The results are shown in Fig. 5, from which it is understood that the composite materials C1 and C2 of the present invention have much larger vibrational damping properties than the prior art composite material C3.

In a third embodiment shown in Fig. 6, three prepreg sheets 1 and four prepreg sheets 5 are laminated in turn and moulded into an integral body by a hot-press method. The carbon fiber fabrics 2 and the ordinary epoxy resin 4 used in the first and the second embodiments are used in the same manner in this third embodiment, wherein however a different constrained type vibrational damping resin produced by using a bisphenol A type epoxy resin as a base and adding thereto a monoepoxy resin so that the glass transition temperature may be adjusted to a room temperature is used. This constrained type vibrational damping resin has an elastic modulus of about 1 Kgf/mm^2 and a mechanical resin has an elastic modulus of abour 1 Kgf/mm^2 and a mechanical loss tan δ of about 1.3 at a room temperature.

As to the composite material C4 obtained in this third embodiment and a prior art composite material C5 produced in the similar manner but from only seven sheets of the prepreg sheet 5 shown in Fig. 2, frequency characteristic curves of loss factors are determined as in the first and the second embodiments. The results are shown in Fig. 7, from which it is understood that the composite material C4 of the present invention has much larger vibrational damping properties than the prior art composite material C5.

In a fourth embodiment shown in Fig. 8, prepreg sheets 11 are those produced by impregnating unidirectionally aligned carbon fibers (sold by Toray Industries, Inc. under trade name Torayca T800) with a constrained type vibrational damping epoxy resin based upon a polyether type epoxy resin (diglycidyl ether of branched alkanediol oligomer) and semi-hardening the epoxy resin by means of an acid anhydride; and prepreg sheets 15 are those produced by impregnating the same carbon fibers with an ordinary epoxy resin (sold by Toray Industries, Inc. under trade name #2500) and semi-hardening the epoxy resin. Two prepreg sheets 11 are sandwiched between upper three prepreg sheets 15 and lower three prepreg sheets 15 and the dirertions of the carbon fibers in these total eight prepreg sheets are varied to have angles of 0°, +45°, -45° and 90° as shown in Fig. 8.

As to the composite material C6 obtained in this fourth embodiment and a prior art composite material C7 produced in the similar manner but from only eight sheets of the prepreg sheet 15, frequency characteristic curves of loss factors are determined as in the first to third embodiments. The results are shown in Fig. 9, from which it is understood that the composite material C6 of the present invention has much larger vibrational damping properties than the prior art composite material C7.

As to the composite materials C6 and C7, tensile strength is determined by using test slips of 25 mm width. The results are 2,480 Kgf for the composite material C6 (fluctuation coefficient showing dispersion = 3.2 %) and 2,510 Kgf for the composite material C7 (fluctuation coefficient = 5.7 %). It is understood that the composite material C6 of the present invention has a tensile strength comparable with that of the prior art composite material C7 and a fluctuation coefficient smaller than that of the prior art composite material C7 and so has improved reliability.

In the above embodiments, carbon fibers are used as the reinforcing fibers. It is however also possible to use inorganic fibers such as glass fibers or organic fibers such as aramid fibers and obtain similar effects.

As explained in detail as above, the present invention has enabled to present a fiber reinforced composite material having a large vibration damping property, which is very useful to solve the problems of troubles of loaded apparatus and lowering of precision of antenna positions in a space construction equipment such as an artificial satellite, and noises in an automobile.

Claims

1. A fiber reinforced composite material comprising:
   (a) at least one composite material layer, which comprises reinforcing fibers impregnated in a constrained type vibrational damping resin material, and
   (b) at least one composite material layer, which comprises reinforcing fibers impregnated in a resin material other than said constrained type vibrational damping resin material;
   said composite material layers (a) and (b) being laminated and integrated.

2. The fiber reinforced composite material according to claim 1, wherein reinforcing fibers are inorganic reinforcing fibers such as carbon fibers or glass fibers or organic reinforcing fibers such as aramid fibers.

3. A prepreg sheet for a fiber reinforced composite material comprising a layer of a composite material prepared by impregnating reinforcing fibers in a constrained type vibrational damping resin material and semi-hardening the resin material.

4. The prepreg sheet according to claim 3, wherein reinforcing fibers are inorganic reinforcing fibers such as carbon fibers or glass fibers or organic reinforcing fibers such as aramid fibers.

FIG. 1

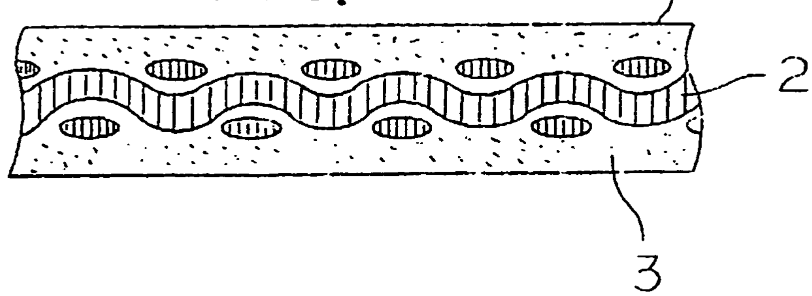


FIG. 2

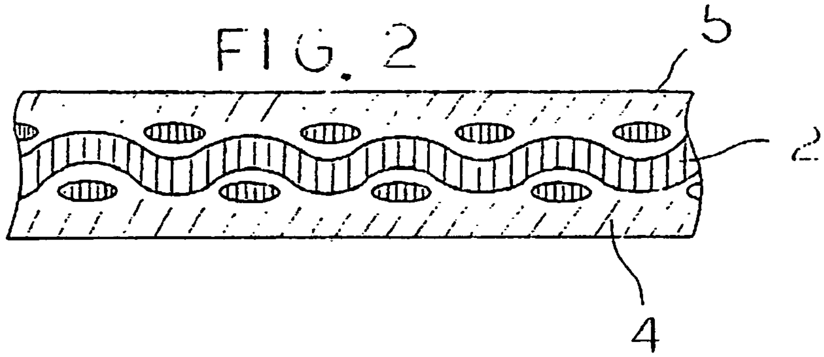


FIG. 3

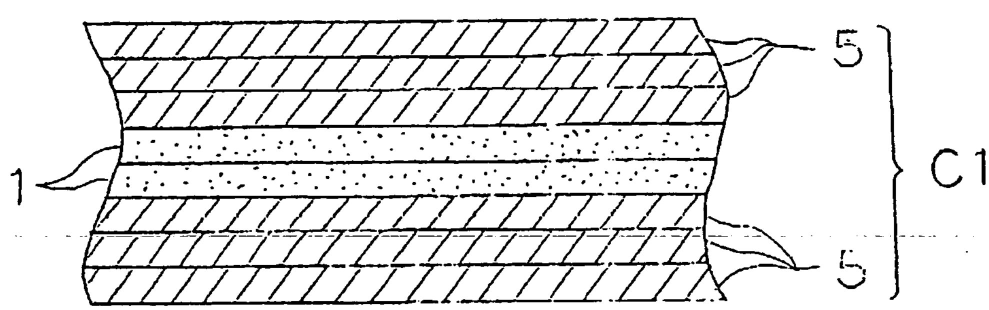


FIG. 4

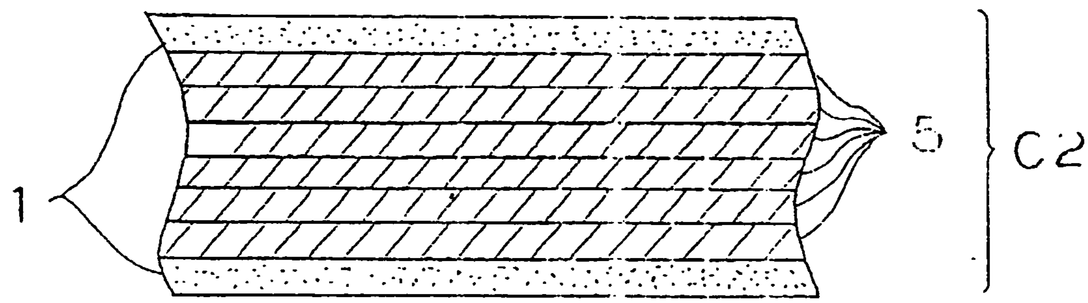


FIG. 5

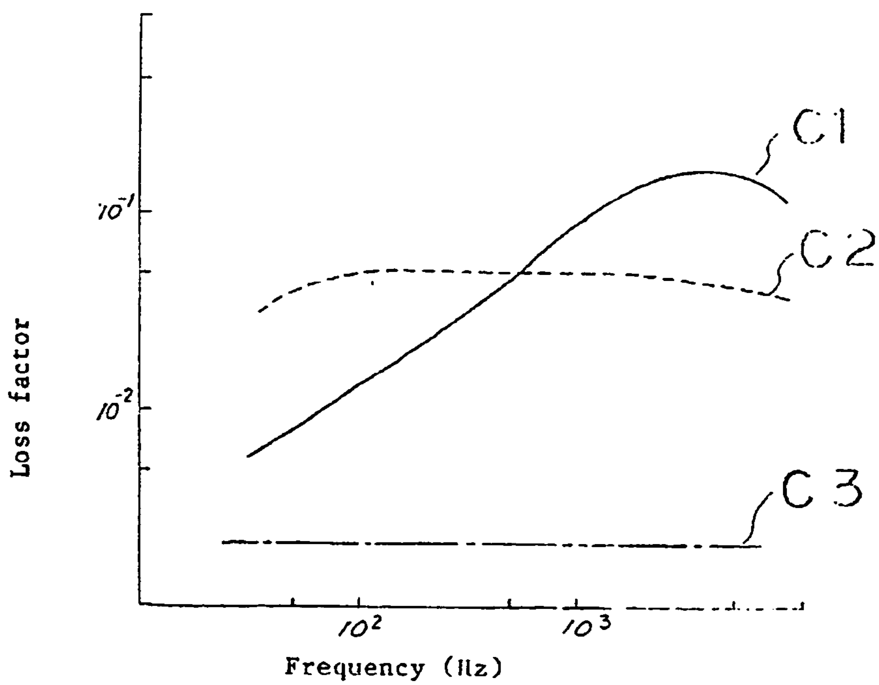


FIG. 6

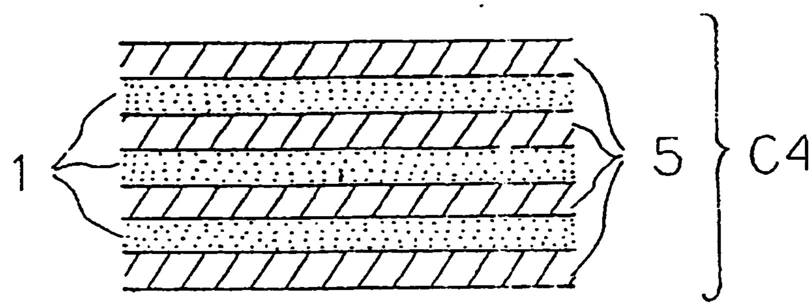


FIG. 7

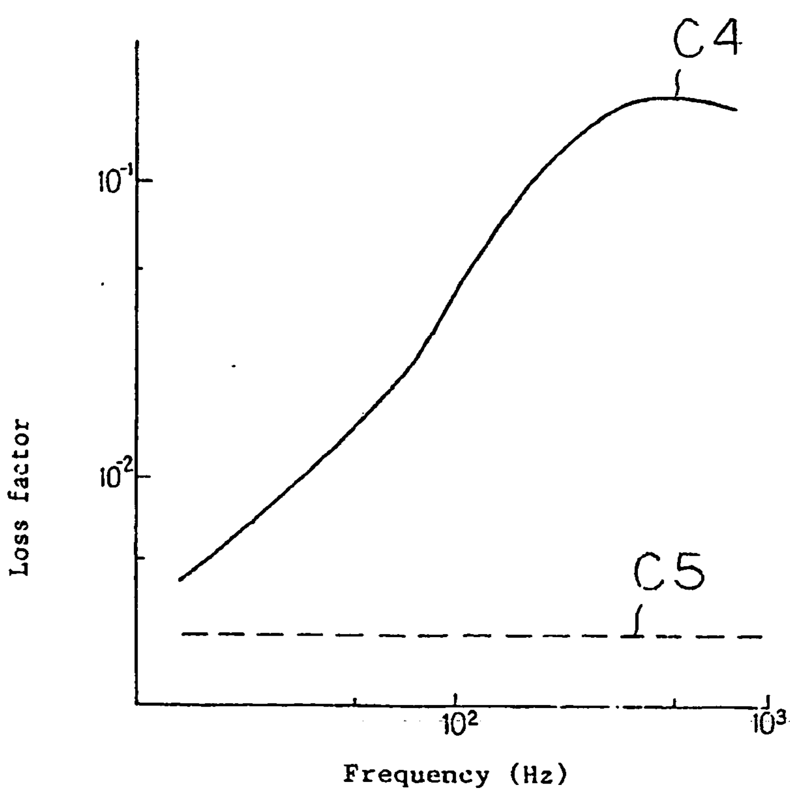


FIG. 8

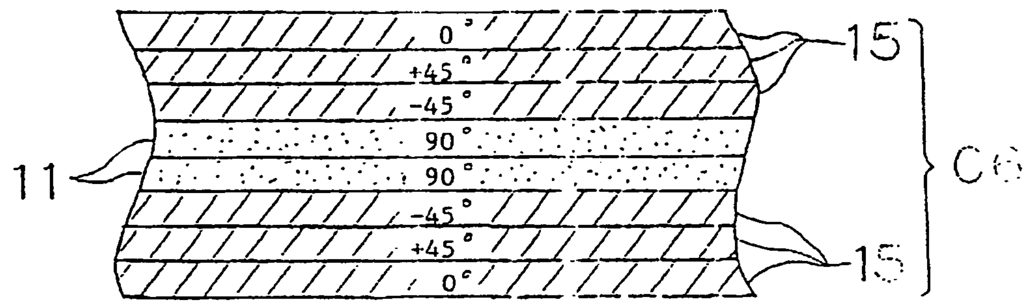

0°
+45°
-45°
90°
90°
-45°
+45°
0°
15
15
11
C6

FIG. 9

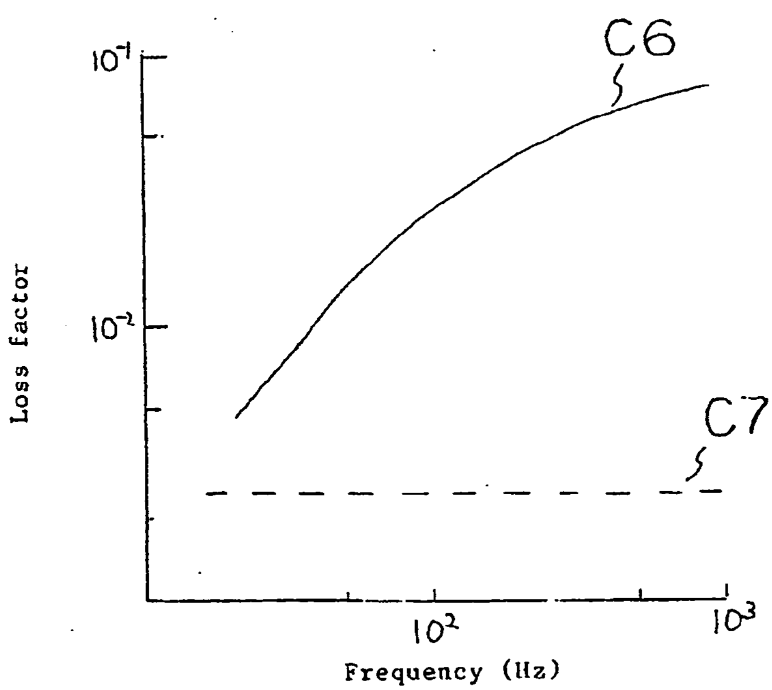

C6
C7
10^{-1}
10^{-2}
Loss factor
10^{2}
10^{3}
Frequency (Hz)

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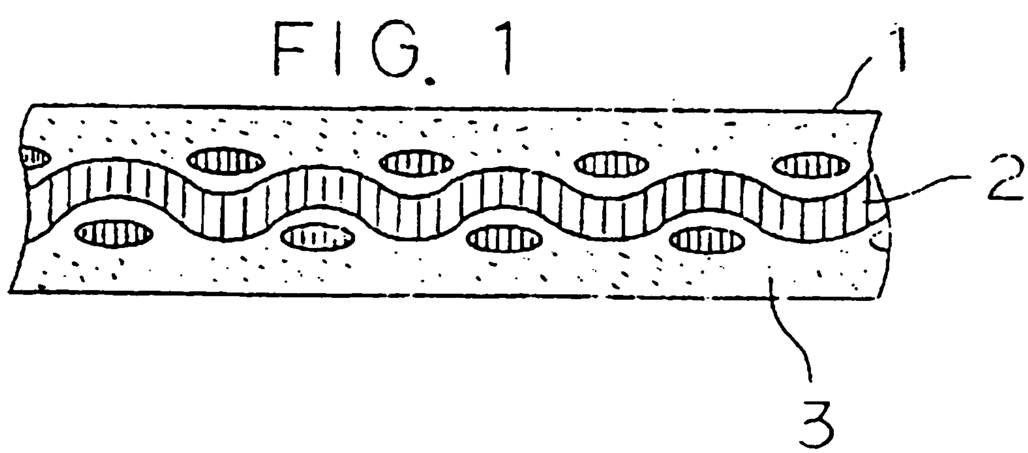
FIG. 1



EP 0 439 197 A3

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EUROPEAN SEARCH REPORT

Application Number

EP 91 10 1000

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 294 232 (SHIN-KOBE ELECTRIC MACHINERY) * abstract * * * page 2, line 1 - page 3, line 65; claims * *	1-4	B 32 B 5/26 B 32 B 5/28
D,Y	EP-A-0 299 086 (MITSUI PETROCHEMICAL & NEC CORPORATION) * page 1 - page 7 * * * page 23, line 18 - line 25; claims * *	3,4	
Y	US-A-4 524 107 (MARCHETTI ET AL) * the whole document * *	3,4	
A	US-A-4 091 160 (KOSS) * the whole document * *	3,4	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B 32 B
C 08 J

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	04 November 91	DE JONGE S.J.P.

CATEGORY OF CITED DOCUMENTS

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